Facile Synthesis of Useful Carboxylic Acids by Electrochemical Carboxylation

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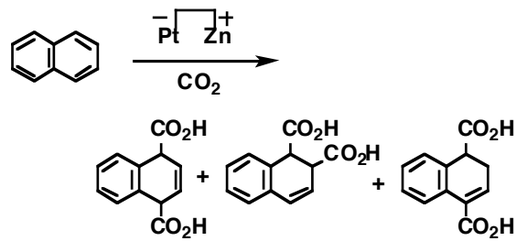
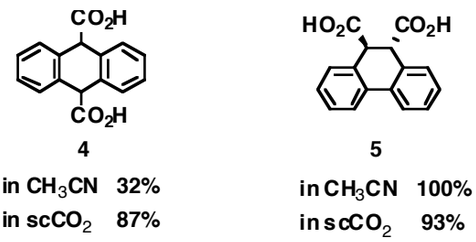
Electrochemical fixation of carbon dioxide is a useful and attractive method for efficient synthesis of various carboxylic acids. We previously reported that electrochemical carboxylation of allylic and propargylic halides, vinyl bromides, vinyl triflates,[1] and phenyl-substituted alkenes proceeded efficiently to give the corresponding carboxylic acids in high yields when a magnesium metal was used as a sacrificial anode.[2] In this paper, we report facile synthesis of arenedicarboxylic acids and cyclic β-alkoxyl- or cyclic β-amino-α,β-unsaturated carboxylic acids by electrochemical carboxylation of polyaromatic compounds and lactone or lactam enol triflates.

Synthesis of Arenedicarboxylic Acids

Electrochemical carboxylation of naphthalene in acetonitrile containing 0.1M Et_4NClO_4 with a Pt cathode and a Zn anode under an atmospheric pressure of carbon dioxide gave two dicarboxylic acids **1** and **2** in 89% and 11% yields, respectively. When this electrolysis was carried out in supercritical carbon dioxide ($scCO_2$; 40 °C, 7.5 MPa), acids **1**, **2**, and **3** were obtained in 53, 29, and 18% yields (Scheme 1). On the other hand, dicarboxylic acids **4** and **5** were obtained in high yields as a single product by similar electrochemical carboxylation of anthracene and phenanthrene, respectively (Scheme 2). Electrolysis of anthracene under supercritical conditions of carbon dioxide ($scCO_2$) gave **4** in 87% yield, although the similar electrolysis in acetonitrile solution in the presence of atmospheric CO_2 gave a lower yield of **4** due to low solubility of anthracene in acetonitrile. Other results will also be reported.



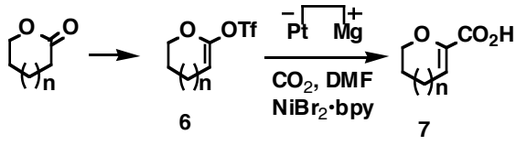
Scheme 1



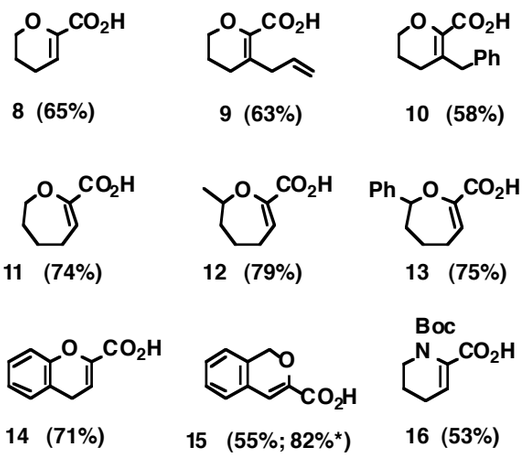
Scheme 2

Synthesis of Captodative Cycloalkenes[3]

Lactone or lactam enol triflates were readily prepared from the corresponding lactone or lactam. Electrochemical carboxylation of lactone enol triflates (**6**) in DMF containing 20 mol% of $NiBr_2 \cdot bpy$ with a Pt cathode and Mg anode under an atmospheric pressure of CO_2 gave cyclic β-alkoxyl-α,β-unsaturated acids (**7**), captodative cycloalkene, in good yields (Scheme 3). These alkenes are useful as synthetic intermediates. Various cyclic β-alkoxyl-α,β-unsaturated acids **8**-**15** and cyclic β-amino-α,β-unsaturated acid **16** were obtained in the yields shown in Scheme 4. In the case of **15**, electrolysis in the absence of Ni catalyst gave a higher yield (82%) of the product.



Scheme 3



[* Yield in the absence of Ni catalyst]

Scheme 4

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2) Senboku, H.; Komatsu, H.; Fujimura, Y.; Tokuda, M. *Synlett*. **2001**, 418 and references cited therein.

3) Senboku, H.; Kanaya, H.; Tokuda, M. *Synlett*.**2002**, 140.